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14. ABSTRACT A detailed knowledge of how the ions transport through the membrane is needed in order to understand how it affects the ionic conductivity and stability of anion exchange membranes. Predictive tools have been created for hydroxide ions transporting through the membrane, however models are needed for predicting carbonate ion transport. Building on this knowledge from hydroxide ion transport, models will be developed to predict carbonate ion transport by using theory as well as experiments. A theoretical approach based on the dusty fluid model (DFM)					
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Report Title

Predicting Carbonate Ion Transport in Alkaline Anion Exchange Materials

ABSTRACT

A detailed knowledge of how the ions transport through the membrane is needed in order to understand how it affects the ionic conductivity and stability of anion exchange membranes. Predictive tools have been created for hydroxide ions transporting through the membrane, however models are needed for predicting carbonate ion transport. Building on this knowledge from hydroxide ion transport, models will be developed to predict carbonate ion transport by using theory as well as experiments. A theoretical approach based on the dusty fluid model (DFM) will be developed to describe the carbonate ion transport. The DFM has been successfully used to predict transport in anion exchange membranes where it can describe hydroxide ion transport. Using this theory, the effects of carbonate ions in the AEM can be studied based on how ions transport through the membrane. Theoretical results were validated using experimental facilities constructed at the University of Connecticut (Storrs, CT) and the Army Research Laboratory (Adelphi, MD) to measure ionic conductivity and carbonate ion flux of the membrane. By exposing one side of a membrane to carbon dioxide, the carbonate flux was measured as well as the ionic conductivity of the membrane. The results were compared with the theoretical solutions for validation.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received

Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received

Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1. A. M. Kiss, T. D. Myles, K. N. Grew, A. A. Peracchio, G. J. Nelson and W. K. S. Chiu, "Carbonate and Bicarbonate Ion Transport in Alkaline Anion Exchange Membranes," Journal of the Electrochemical Society, 2013.
2. Wilson K. S. Chiu, "Part 1. Role of the 3-D Electrode Microstructure on Charge Transfer, Mass Transfer, and Electrochemical Reactions in Solid Oxide Fuel Cells; Part 2. Ion and Water Transport in Alkaline Anion Exchange Membranes," technical seminar for the Army Research Laboratory (host: Dr. Deryn Chu), Adelphi, MD, August 13, 2012.

Number of Presentations: 2.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

01/30/2013 2.00 Andrew M. Kiss, Timothy D. Myles, Kyle N. Grew, Aldo A. Peracchio, George J. Nelson, and Wilson K. S. Chiu. Carbonate and Bicarbonate Ion Transport in Alkaline Anion Exchange Membranes, 222nd Meeting of the Electrochemical Society. 2012/10/10 00:00:00, . : ,

01/30/2013 3.00 Andrew M. Kiss, Timothy D. Myles, Kyle N. Grew, Aldo A. Peracchio, George J. Nelson, and Wilson K. S. Chiu. Predicting Carbonate Species Ionic Conductivity in Alkaline Anion Exchange Membranes, 45th Power Sources Conference. 2012/06/11 00:00:00, . : ,

TOTAL: 2

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

01/30/2013 1.00 A. M. Kiss, T. D. Myles, K. N. Grew, A. A. Peracchio, G. J. Nelson and W. K. S. Chiu. Carbonate and Bicarbonate Ion Transport in Alkaline Anion Exchange Membranes, Journal of the Electrochemical Society (02 2013)

TOTAL: 1

Number of Manuscripts:

Books

Received Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

1. . During Tim Myles ARL apprenticeship this past summer, he was competitively selected to represent ARL's Electrochemistry branch to present at the Sixth Annual U. S. Army Research Laboratory (ARL) Summer Student Symposium.
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2. The PI, Prof. Wilson Chiu, was elected to the Connecticut Academy of Science and Engineering in March 2013.
-

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Andrew Kiss	1.00	
Timothy Myles	1.00	
FTE Equivalent:	2.00	
Total Number:	2	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Wilson K. S. Chiu	0.30	
FTE Equivalent:	0.30	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics	
This section only applies to graduating undergraduates supported by this agreement in this reporting period	
The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):.....	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PhDs

<u>NAME</u>
Total Number:

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attachment.

Technology Transfer

Project Title: Predicting Carbonate Ion Transport in Alkaline Anion Exchange Materials

PI/Institution: Wilson K. S. Chiu, Professor, Department of Mechanical Engineering, University of Connecticut

Period of Performance:

Type of Award: X Research Instrumentation

OBJECTIVE(S): (100 words maximum)

The goal of this project is to understand carbonate ion transport in alkaline anion exchange materials. Numerical models along with detailed experiments will be used to describe carbonate ion transport and its effect on the ionic conductivity and stability of anion exchange membranes (AEM).

APPROACH: (One-to-two paragraph description of approach taken to accomplish objective(s)).

A detailed knowledge of how the ions transport through the membrane is needed in order to understand how it affects the ionic conductivity and stability of anion exchange membranes. Predictive tools have been created for hydroxide ions transporting through the membrane, however models are needed for predicting carbonate ion transport. Building on this knowledge from hydroxide ion transport, models will be developed to predict carbonate ion transport by using theory as well as experiments. A theoretical approach based on the dusty fluid model (DFM) will be developed to describe the carbonate ion transport. The DFM has been successfully used to predict transport in anion exchange membranes where it can describe hydroxide ion transport. Using this theory, the effects of carbonate ions in the AEM can be studied based on how ions transport through the membrane. Theoretical results were validated using experimental facilities constructed at the University of Connecticut (Storrs, CT) and the Army Research Laboratory (Adelphi, MD) to measure ionic conductivity and carbonate ion flux of the membrane. By exposing one side of a membrane to carbon dioxide, the carbonate flux was measured as well as the ionic conductivity of the membrane. The results were compared with the theoretical solutions for validation.

SUMMARY: (Text, figures, tables, and images that provide major accomplishments of project. Entire document not to exceed three single-spaced pages.)

Carbonate Ion Transport Model

Andrew Kiss, graduate student, is leading the development of a numerical model and experiments to predict carbonate transport in AEMs. He began with a diffusion model that included the membrane as an interacting species named the dusty fluid model (DFM). With this model, an expression to solve for the ionic conductivity of the membrane can be derived which is a function of several important parameters such as diffusion coefficients and free ion concentrations. The diffusion coefficient of the ion in

the membrane is difficult to quantify since it is a strong function of the local hydration of the membrane. A diffusion coefficient for water in the membrane was experimentally measured using a permeation based water flux setup at the University of Connecticut. To arrive at an ion-membrane diffusion coefficient, principles from kinetic theory are used to scale the existing water-membrane diffusion coefficient to the desired ion form. The scaling by kinetic theory allows ion-membrane diffusion coefficients to be calculated with the knowledge of ion properties, such as mass and hydrated radius, and total ion concentration. The concentration of free ions in the membrane is based on equilibrium chemistry and can be fitted to best match experimental results, as shown in Figure 1.

Applying this theory to a SnowPure Excellion I-200 AEM, the effect of carbonate can be observed in Figure 2. Carbonate and bicarbonate have lower diffusion coefficients than hydroxide. Hydroxide has a small mass and hydrated radius compared to the other ions and based on kinetic theory should have the largest diffusion coefficient. Two experiments were performed with this membrane: one with the membrane in the hydroxide ion form, and one with a mixed carbonate/bicarbonate form. Solving for ionic conductivity in the hydroxide form, it can be seen that the ionic conductivity of the membrane is greatest. The mixed carbonate form saw a decrease in performance which is attributed to several factors including a lower ion diffusion coefficient and lower free ion dissociation. These results were presented at two technical conferences [1,2] and a journal manuscript is currently being prepared [3].

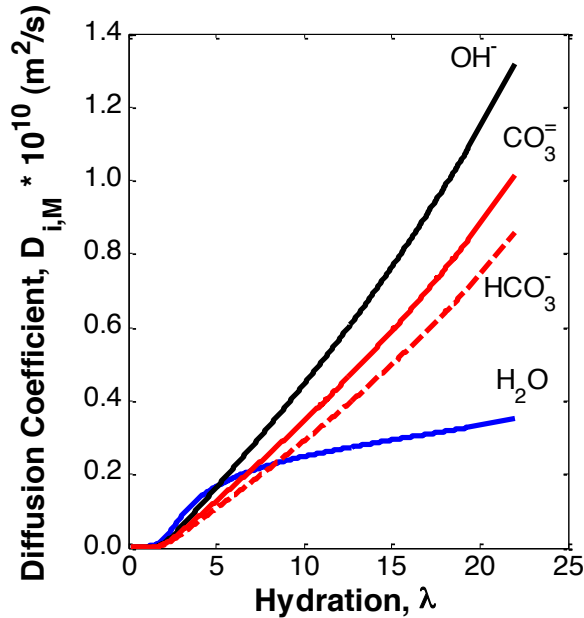


Figure 1. Ion-membrane diffusion coefficients predicted using experimentally measured water-membrane diffusion coefficient in SnowPure Excellion I-200 AEM.

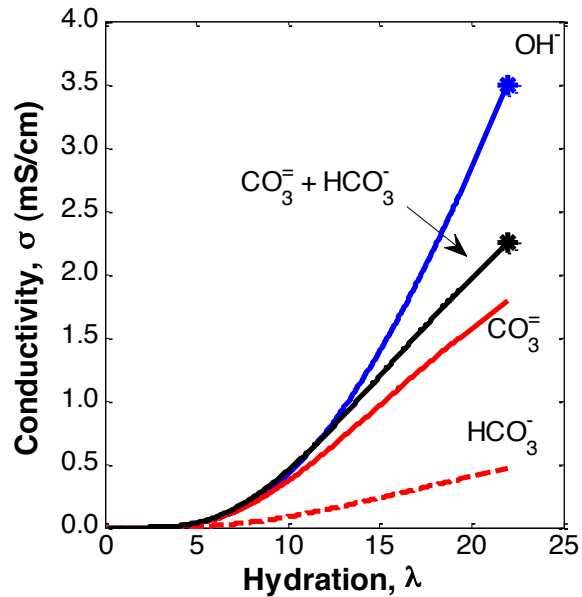


Figure 2. Individual contributions and total ionic conductivities for the in SnowPure Excellion I-200 AEM in hydroxide and mixed carbonate/bicarbonate form. Symbols are experimental results from Vega et al. [4].

Experimental Measurement of Carbonate Ion Flux

Timothy Myles, graduate student, was selected to participate in the "Science and Engineering Apprenticeship Program – College Qualified Leaders (SEAP-CQL)" at the Army Research Laboratory (Adelphi, MD) for 10 weeks during Summer 2012 under Dr. Xiaoming Ren's mentorship. During this apprenticeship, Tim Myles obtained and analyzed data from carbon dioxide flux experiments for Nafion 117 and Tokuyama A201 anion exchange membranes. The flux experiments were designed and performed at the Army Research Laboratory (ARL) in Adelphi, MD. The basic design of the experimental procedure used to investigate CO₂ cross over involves a permeation cell as described in the schematic shown in Figure 3a. In the setup N₂ (Airgas Ultra High Purity Nitrogen) is passed on one side of the cell and CO₂ (Air Products UN-1013) is passed on the other. The partial pressure difference of CO₂ results in transport through the membrane. The CO₂ which enters the N₂ stream is then detected by an IR based detector (Horiba VIA-510) which records the transient response. Various operational parameters were controlled through the use of the Fuel Cell Technologies Test Station such as the relative humidity and flow rate of the feed gases, the cell temperature, and the pressure of the CO₂ stream. Valve #1 and Valve #2 shown in the schematic were used to control the CO₂ exposure of the cell.

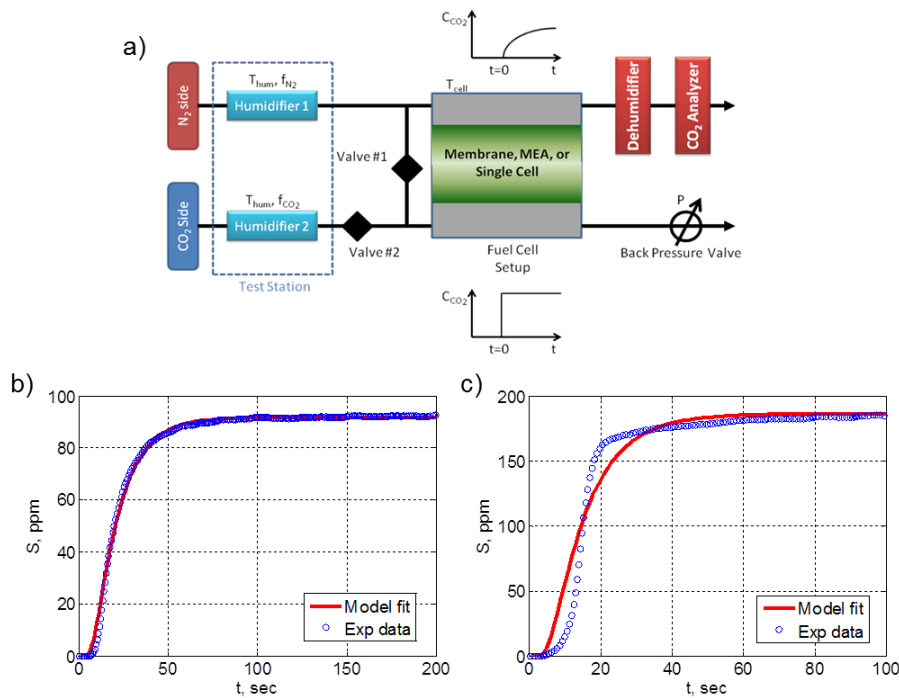


Figure 3. (a) Schematic of the permeation cell experiment used to measure transient CO₂ flux across the polymer electrolyte membrane. Experimental result vs. model trend for transient CO₂ concentration detected in the N₂ stream using the (b) Nafion 117 membrane (30°C, 100% RH), and the (c) Tokuyama A201 anion exchange membrane (35°C, 100% RH).

The results in Figures 3b and 3c were fitted with a permeation model based on Fick's second law assuming constant diffusivity with diffusivity being the dominate mode of

transport. The model does well in predicting the transient behavior of CO₂ transport in Nafion 117 membrane. It does not fully capture the transient trend for the Tokuyama A201 anion exchange membrane. This result indicates other transport mechanisms are prevalent, some of which are likely linked to facilitated transport due to the presence of carbonate ions. Further modeling development will be performed to elucidate these mechanisms and separate contributions connected to carbonate transport.

During Tim Myles' ARL apprenticeship, he was competitively selected to represent ARL's Electrochemistry branch to present a portion of these results at the Sixth Annual U. S. Army Research Laboratory (ARL) Summer Student Symposium [5]. He also completed a technical report to summarize his work under his 2012 summer apprenticeship [6]. These results will be submitted to the 224th Meeting of the Electrochemical Society, and journal manuscripts are currently being and prepared.

The PI, Prof. Wilson Chiu, visited the Army Research Laboratory (Adelphi, MD) on August 13, 2012. During this visit hosted by Dr. Deryn Chu, Prof. Chiu gave a technical seminar on ion and water transport in anion exchange membrane materials and other technical areas [7], and discussed ongoing collaborations on this project with the Electrochemistry branch. These activities are part of the overall effort to ensure that this STIR project is being communicated to ARL, such as visiting ARL to provide technical seminars and engage in technical discussions, and having a graduate student spend the summer at ARL to conduct experiments of interest to both ARL and this project.

References

1. A. M. Kiss, T. D. Myles, K. N. Grew, A. A. Peracchio, G. J. Nelson and W. K. S. Chiu, "Predicting Carbonate Species Ionic Conductivity in Alkaline Anion Exchange Membranes," Proceedings of the 45th Power Sources Conference, Paper No. 18.22, Las Vegas, NV, June 11-14, 2012.
2. A. M. Kiss, T. D. Myles, K. N. Grew, A. A. Peracchio, G. J. Nelson and W. K. S. Chiu, "Carbonate and Bicarbonate Ion Transport in Alkaline Anion Exchange Membranes," 222nd Electrochemical Society Meeting, Paper No. 3107, Honolulu, HI, October 7-12, 2012.
3. A. M. Kiss, T. D. Myles, K. N. Grew, A. A. Peracchio, G. J. Nelson and W. K. S. Chiu, "Carbonate and Bicarbonate Ion Transport in Alkaline Anion Exchange Membranes," in preparation, 2013.
4. J. A. Vega, C. Chartier and W. E. Mustain, J. Power Sources., 195, 21 (2010).
5. Timothy Myles, "CO₂ Transport in Nafion and Anion Exchange Membranes," Sixth Annual U. S. Army Research Laboratory (ARL) Summer Student Symposium (Graduate Students), Adelphi, MD, 2012.
6. Timothy Myles and Xiaoming Ren, "CO₂ Transport in Nafion and Anion Exchange Membranes," U. S. Army Research Laboratory Summer Research Technical Report, Science and Engineering Apprenticeship Program – College Qualified Leaders (SEAP-CQL), August 2012 (distribution limited to DoD and U.S. DoD contractors only).
7. Wilson K. S. Chiu, "Part 1: Role of the 3-D Electrode Microstructure on Charge Transfer, Mass Transfer, and Electrochemical Reactions in Solid Oxide Fuel Cells; Part 2: Ion and Water Transport in Alkaline Anion Exchange Membranes," technical seminar, Army Research Laboratory, Adelphi, MD, August 13, 2012.